

## TITLE OF THE INVENTION

Crystallization of Adipic Acid from its Solution in Aqueous Nitric Acid

## FIELD OF THE INVENTION

The invention relates to crystallization of adipic acid from its  
5 solution in aqueous nitric acid and especially to the recovery of adipic acid  
from the product of oxidation of cyclohexanol and cyclohexanone by  
aqueous nitric acid

## BACKGROUND OF THE INVENTION

Adipic acid is commercially produced by the oxidation of  
10 cyclohexanol and cyclohexanone by concentrated nitric acid. Initial  
product recovery and purification are accomplished through crystallization  
of the reaction mixture followed by solid-liquid separation. Additional  
purification of adipic acid is accomplished through one or more steps of  
aqueous recrystallization followed by solid-liquid separation. The reaction  
15 of cyclohexanol and cyclohexanone with nitric acid produces adipic acid  
with several byproducts, e.g. glutaric acid, succinic acid, of varying  
concentrations. In order to produce adipic acid of good quality, a major  
part of the purification needs to be accomplished during the initial product  
recovery through crystallization of the reaction mixture from the nitric acid  
20 oxidation step.

For crystallization of adipic acid from the solution obtained from the  
oxidation of cyclohexanol and cyclohexanone by nitric acid, it has  
generally been observed that the higher the temperature of crystallization,  
the purer the product of crystallization. However, the mother liquor from  
25 crystallization at high temperature contains a high concentration of adipic  
acid. In order to prevent loss of adipic acid with the mother liquor of  
crystallization, most refining processes in commercial practice require that  
this crystallization be conducted at a low temperature, typically below 60  
degrees C. As a result, the product obtained contains substantial impurity  
30 that requires significant additional refining. It would, therefore, be  
beneficial to have a process to achieve the benefit of high temperature  
crystallization without excessive product loss in the mother liquor.

## SUMMARY OF THE INVENTION

In the present invention, the crystallization is conducted in a plurality of crystallization stages in decreasing order of operating temperature beginning with a first crystallizer and ending with a final  
5 crystallizer. Each crystallizer is operated in a continuous mode of operation. A feed solution is introduced in the first crystallizer and a product slurry is withdrawn from the final crystallizer. The temperature of the first crystallizer should be such that it is significantly higher than the temperature of the final crystallizer, yet a substantial concentration of solid  
10 particles is achieved in the first crystallizer in order to alleviate the detrimental effect of low solids concentration in the first stage crystallizer.

The present invention, therefore, is a process for the crystallization of an adipic acid-containing oxidation product produced by the nitric acid oxidation of cyclohexanone (K) and cyclohexanol (A), said oxidation  
15 product comprising adipic acid, glutaric acid and nitric acid, said process comprising,

introducing into a first crystallizer said oxidation product, said crystallizer providing a first crystallization temperature sufficient to produce a first crystallizer product comprising a first mother liquor and a first  
20 harvest of solid crystals, said solid crystals being present at a concentration of at least about 10 weight percent based on the combined weight of the mother liquor and the crystals;

introducing the first crystallizer product into a second crystallizer providing a second crystallizer temperature lower than said first  
25 temperature to produce a second crystallizer product comprising a second mother liquor and a second harvest of solid crystals, said second mother liquor having a lower concentration of adipic acid than said first mother liquor and said second harvest of solid crystals having a greater weight percent of adipic acid than said first harvest; and

30 either

harvesting the solid crystals from the second crystallizer if the concentration of adipic acid in solution in the second mother liquor is less than or equal to a pre-selected concentration in the range of about 2 to 12 weight percent of the weight of the second mother liquor, or, if the

concentration of adipic acid in solution in the second mother liquor is higher than said pre-selected concentration in the range of about 2 to 12 weight percent of the weight of the second mother liquor, then

introducing the second crystallizer product into one additional  
5 crystallizer or a plurality of additional crystallizers in series providing successively lower crystallization temperatures until a final crystallization product comprising a final mother liquor and a final harvest of solid crystals is produced in which the concentration of adipic acid in solution in the final mother liquor is less than or equal to said pre-selected  
10 concentration in the range of about 2 to 12 weight percent of the weight of the final mother liquor, and

harvesting the solid crystals from the final crystallization product.

#### BRIEF DESCRIPTION OF THE DRAWING

The drawing consists of three figures. Figure 1 depicts a block  
15 diagram of a process embodying the present invention involving only two stages in the crystallization process. Figure 2 depicts a block diagram of one embodiment of the present invention in which at least a portion of an adipic acid-containing oxidation product is premixed with a first crystallizer product and then introduced into the first crystallizer. Figure 3 shows a  
20 block diagram of another embodiment of the present invention in which at least a portion of an adipic acid-containing oxidation product is premixed with a second crystallizer product and then introduced into the second crystallizer.

#### DETAILED DESCRIPTION OF THE INVENTION

25 Referring now to Figure 1, there is shown a block diagram illustrating apparatus that embodies one embodiment of the present invention involving only two stages in the crystallization process, namely, a first crystallizer and a second crystallizer.

An adipic acid-containing oxidation product (12) produced by the  
30 nitric acid oxidation of cyclohexanone (K) and cyclohexanol (A) is continuously fed into a first crystallizer (20). In the first crystallizer, the oxidation product is cooled down to a first crystallization temperature. The cooling action causes crystallization of adipic acid in solution in the oxidation product that is fed to the first crystallizer to produce a first

crystallizer product comprising a first mother liquor and a first harvest of solid crystals. The first crystallization temperature should be low enough to allow enough adipic acid in solution in the oxidation product to crystallize so that the concentration of solid crystals in the first crystallizer is at least about 10 weight percent based on the combined weight of the mother liquor and the crystals in the first crystallizer. A portion of the first crystallizer product (28) is continuously withdrawn from the first crystallizer and fed to a second crystallizer (30).

The first crystallizer product is further cooled down in the second crystallizer to a second crystallization temperature. Cooling action in the second crystallizer causes crystallization of adipic acid in solution in the first mother liquor associated with the first crystallizer product that is fed to the second crystallizer to produce a second crystallizer product comprising a second mother liquor and a second harvest of solid crystals. The second crystallization temperature is selected in a way that the concentration of adipic acid in solution in the second mother liquor is less than the concentration of adipic acid in solution in the first mother liquor and is less than or equal to a pre-selected concentration in the range of about 2 to 12 weight percent of the weight of the second mother liquor. The concentration of solid crystals in the second crystallizer product is, therefore, higher than the concentration of solid crystals in the first crystallizer product. A portion of the second crystallizer product (34) is continuously withdrawn from the second crystallizer and is processed through a solid-liquid separation unit (not shown) to harvest the solid crystals.

If the concentration of adipic acid in solution in the second mother liquor is higher than said pre-selected concentration, the second crystallizer product stream (34) can be fed to a final crystallizer or to a plurality of additional crystallizers in series ending in a final crystallizer (not shown) and providing successively lower crystallization temperatures until a final crystallization product comprising a final mother liquor and a final harvest of solid crystals is produced. The final crystallization temperature should be selected in a way that the concentration of adipic acid in solution in the final mother liquor is less than the concentration of adipic

acid in solution in any preceding stage mother liquor and is less than or equal to said pre-selected concentration in the range of about 2 to 12 weight percent of the weight of the final mother liquor. The concentration of solid crystals in the final crystallizer product is, therefore, higher than  
5 the concentration of solid crystals in any preceding crystallizer product. A portion of the final crystallizer product (not shown) is continuously withdrawn from the final crystallizer and is processed through a solid-liquid separation unit (not shown) to harvest the solid crystals.

Generally it is not advantageous to use more than three stages of  
10 crystallization and in many cases two stages of crystallization provides adequate benefit.

The oxidation mixture is generally hot and unsaturated, typically containing about 15 to 25% adipic acid and typically at a temperature in the range of about 75 to 95 degrees C. Typically about 25 to 45% nitric  
15 acid, about 5 to 15 wt% glutaric acid and about 2 to 10 wt% succinic acid are present in the oxidation product. On the basis of combined weight of water and nitric acid only, the concentration of nitric acid should be in the range of about 45 to 55 wt%.

The first crystallizer is an enclosed vessel in which a constant  
20 volume of the first crystallizer product should be maintained. It is equipped with an agitation device (21) in order to keep a uniform suspension of solids in the mother liquor in the entire crystallizer. Optionally, a draft tube (not shown) can be installed inside the crystallizer. Cooling is generally accomplished by evaporating at a sub-atmospheric  
25 pressure a portion the water and nitric acid (i.e. the solvent) contained in the oxidation product. A continuous flow of vapor (22) leaves the top of the crystallizer.

The concentration of solids in the first crystallizer should be at least 10 wt% based on the total weight of the first crystallizer product. A high  
30 solids concentration is beneficial for crystallizer operation and for purity of final product. The concentration of solids in the first crystallizer can be increased by increasing the concentration of adipic acid in the oxidation product fed to the first crystallizer, decreasing the first crystallizer temperature, introducing solid adipic acid crystals, e.g. from a second

crystallizer product, operating the first crystallizer in a double draw-off (DDO) mode. In the DDO mode of operation, a stream of crystallizer content, called overflow, comprising preferentially small particles is withdrawn simultaneously with a stream of crystallizer content, called  
5 underflow, comprising particles of all sizes. This action increases concentration of solid particles in the crystallizer.

The first crystallizer can be a single vessel or multiple vessels in parallel (not shown). A residence time of about 15 to 150 minutes (based on the total flow rate of the oxidation product fed to the first crystallizer)  
10 should be allowed for the first crystallizer (for each vessel if multiple vessels in parallel are used). In order to prevent flashing of any solvent, there should be adequate liquid height above the location at which the oxidation product is introduced in the crystallizer and there should be adequate mixing.

15 The second crystallizer is an enclosed vessel in which a constant volume of the second crystallizer product should be maintained. It is equipped with an agitation device (31) in order to keep a uniform suspension of solids in the mother liquor in the entire crystallizer. Optionally, a draft tube (not shown) can be installed inside the crystallizer.  
20 Cooling is generally accomplished by evaporating at a sub-atmospheric pressure a portion of the water and nitric acid (i.e. solvent) contained in the first crystallizer product. A continuous flow of vapor (32) leaves the top of the crystallizer. A portion of the second crystallizer product (34) is continuously withdrawn from the second crystallizer.

25 The concentration of solids in the second crystallizer product is greater than the concentration of solids in the first crystallizer product, i.e. greater than about 10 wt% based on the total weight of the second crystallizer product. The second crystallizer temperature should be in the range of about 30 to 60 degrees C. The concentration of adipic acid in the  
30 second mother liquor should be in the range of about 2 to 12 wt%.

The second crystallizer can be a single vessel or multiple vessels in parallel (not shown). A residence time of about 15 to 150 minutes (based on the total flow rate of the first crystallizer product fed to the second crystallizer) should be allowed for the second crystallizer (for each vessel

if multiple vessels in parallel are used). In order to prevent flashing of any solvent, there should be adequate liquid height above the location at which the first crystallizer product is introduced in the crystallizer and there should be adequate mixing.

5           The third or any subsequent stage crystallizer can be designed and operated in a way similar to the second crystallizer as described above. The preselected concentration of dissolved adipic acid for the second or any subsequent mother liquor is based on the value that is acceptable for further processing, e.g., recycling the mother liquor.

10           Referring now to Figure 2, there is shown a block diagram illustrating apparatus that embodies an embodiment of the present invention in which at least a portion of the adipic acid-containing oxidation product is premixed with at least a portion of the first crystallizer product and then introduced into the first crystallizer. In this embodiment of the  
15           invention, the flow of adipic acid-containing oxidation product (12) is split into two parts (14) and (16). Stream (14) is directly fed into the first crystallizer. Stream (16) is fed into a first feed pre-mixer vessel (25) where it combines with a flow (24) of the first crystallizer product. A first premixed feed (26) of the above combined streams is withdrawn from the  
20           first pre-mixer vessel and fed into the first crystallizer.

          The first pre-mixer vessel can be a small, enclosed tank or a section of a pipe or an isolated zone inside the crystallizer. It can be operated liquid full and should be designed to accomplish intimate mixing of the streams. It should be advantageous to combine the streams in such  
25           a ratio that the liquor after mixing is slightly unsaturated. For example, 100g of oxidation product containing about 20 wt% adipic acid, about 5 wt% glutaric acid about 5 wt% succinic acid, about 35 wt% nitric acid and about 35 wt% water at 92 degrees C and 100 g of mother liquor obtained from first crystallizer product at 60 degrees C containing about 12 wt%  
30           adipic acid, about 5 wt% glutaric acid about 5 wt% succinic acid, about 39 wt% nitric acid and about 39 wt% water will produce a significantly unsaturated liquor upon mixing intimately.

          Together with an unsaturation in liquor, an adequate residence time should be provided so that at least a portion of the fine particles of adipic

acid might dissolve. For example, for a mixture temperature of about 50 to 75 degrees C, a residence time of about 1 to 5 minutes should be adequate. Optionally, heat can be provided in order to accomplish dissolving of fine particles.

5           Referring now to Figure 3, there is shown a block diagram illustrating apparatus that embodies another embodiment of the present invention in which at least a portion of the adipic acid-containing oxidation product is premixed with at least a portion of the second crystallizer product and then introduced into the second crystallizer. In this  
10           embodiment of the invention, the flow of adipic acid-containing oxidation product (12) is split into two parts (14) and (18). Stream (14) is directly fed into the first crystallizer. Stream (18) is fed into a second feed pre-mixer vessel (35) where it combines with a flow (36) of the second crystallizer product. A second premixed feed (38) of the above combined streams is  
15           withdrawn from the second pre-mixer vessel and fed into the second crystallizer.

          The second pre-mixer vessel can be a small, enclosed tank or a section of a pipe or an isolated zone inside the crystallizer. It can be operated liquid full and should be designed to accomplish intimate mixing  
20           of the streams. It should be advantageous to combine the streams in such a ratio that the liquor after mixing is slightly unsaturated. In addition, an adequate residence time should be provided so that at least a portion of the fine particles of adipic acid might dissolve. For example, for a mixture temperature of about 50 to 75 degrees C, a residence time of about 1 to 5  
25           minutes should be adequate. Optionally, heat can be provided in order to accomplish dissolving of fine particles.

          It may be beneficial to have an arrangement in which at least a portion of the adipic acid oxidation product is premixed with at least a portion of any crystallizer product from a crystallizer subsequent to the  
30           second crystallizer and then introduced into the same crystallizer.